Supporting Information:

Rhodium-Catalyzed Asymmetric Ring Opening of Oxabicyclic Alkenes with Organoboronic Acids

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1. Methods

All reactions were carried out under nitrogen atmosphere with magnetic stirring. THF was distilled under nitrogen atmosphere from benzophenone ketyl prior to use. Boronic acids were obtained from Aldrich and used without further purification. Ethylene glycol esters of boronic acids were synthesized by heating phenylboronic acid (1 eq.) and ethylene glycol (1 eq.) in toluene, and distilling off the toluene/water. The resulting liquid was purified by Kugelrohr distillation. Oxabicycles **1**¹, **4a**, **4b**², **9a**³, and **9b**⁴ were synthesized according to literature procedures. Solvents and solutions were transferred using standard inert atmosphere techniques. Analytical thin layer chromatography was performed with Silicycle™ normal phase 0.25 mm Aluminum-backed TLC plates. Visualization was accomplished with 254 nm UV light and ethanolic anisaldehyde or aqueous potassium permanganate solutions. Purification of reaction products was done by flash chromatography with Silicycle™ Ultra-Pure 230-400 mesh silica gel. ¹H NMR spectra were recorded at 300 or 400 MHz, and ¹³C NMR spectra (proton-decoupled) were recorded at 75 or 100 MHz, using Varian spectrometers and solvent as the internal standard. ¹⁹F NMR was recorded at 282 MHz with chemical shifts relative to CFC1₃ (internal standard). Spectral features are tabulated in the following order: chemical shift (δ, ppm); number of protons; multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); coupling constants (*J*, Hz). IR spectra were obtained using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as a neat film on a NaCl plate. High resolution mass spectra were obtained from a VG 70-250S (double-focusing) mass spectrometer at 70 eV. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. HPLC analysis was performed with an Agilent 1100 series HPLC with photodiode array and Chiracel chiral columns with Uniguard

pre-column filters. Optical rotations were measured in a 10 cm cell with a Perkin-Elmer 243 B polarimeter with sodium lamp and are reported as follows: $[\alpha]_D^{T^\circ\text{C}}$ ($c = \text{g}/100 \text{ mL}$, solvent).

2. Experimental Procedures

Characterization details for compounds made with the following reactions are given in Section 3.

Procedure for the preparation of compound **2**:

A 10 mL flask was charged with $[\text{Rh}(\text{COD})\text{Cl}]_2$ (4.2 mg, 0.0085 mmol), (*R*)-(*S*)- PPF-P(*t*-Bu)₂ ligand **3** (9.4 mg, 0.0173 mmol), and oxabenzonorbornadiene **1** (50 mg, 0.347 mmol). A stir bar was added and the flask was sealed and flushed with nitrogen before distilled THF (3 mL) was added. Phenylboronic acid (ethylene glycol ester, 62 mg, 0.419 mmol) was then added by syringe as a THF solution (with ~0.3 mL THF), followed by Cs_2CO_3 (5M) in H_2O (35 μL). The reaction was stirred for 14 h, after which time TLC analysis (25% EtOAc/hexanes) indicated the reaction was complete. The solvent was then evaporated and the crude was dissolved with DCM and transferred onto a glass column packed with silica gel (~3/4" x 12") and eluted with 5-8% EtOAc/hexanes. Product **2** was isolated as a colourless oil: 60.3 mg, yield = 78%, ee = 93%.

Representative procedure for the preparation of cyclohexenols **5a-5j**:

A 5 mL flask was charged with $[\text{Rh}(\text{COD})\text{Cl}]_2$ (3.3 mg, 0.0067 mmol), (*R*)-(*S*)- PPF-P(*t*-Bu)₂ ligand **3** (7.4 mg, 0.0136 mmol), and 4-methoxyphenylboronic acid (49 mg, 0.322 mmol). A stir bar was added and the flask was sealed and flushed with nitrogen before distilled THF (1 mL) was added. Oxabicyclic **4a** (50 mg, 0.271 mmol) was added to the reaction by syringe as a

THF solution (with ~0.3 mL THF). Cs₂CO₃ (5M) in H₂O (27 µL, 0.136 mmol Cs₂CO₃) was added by syringe and the reaction was stirred for 14 h. The solvent was then evaporated and the crude was dissolved with DCM and transferred onto a glass column packed with silica gel (~3/4" x 7") and eluted with 5-20% EtOAc/hexanes. Product **5i** was isolated as a colourless oil: 69.1 mg, yield = 87%, ee = 96%.

Procedure for the preparation of compound **6**:

A 10 mL flask was charged with [Rh(COD)Cl]₂ (2.5 mg, 0.00507 mmol), (*R*)-(-*S*)- PPF-P(*t*-Bu)₂ ligand **3** (5.5 mg, 0.0101 mmol), oxabicycle **4b** (80 mg, 0.202 mmol), and *trans*-1-hexen-1-ylboronic acid (31 mg, 0.242 mmol). A stir bar was added and the flask was sealed and flushed with nitrogen before distilled THF (1 mL) and Cs₂CO₃ (5M) in H₂O (20 µL, 0.100 mmol Cs₂CO₃) were added by syringe. The reaction was stirred for 14 h, after which time TLC analysis (20% EtOAc/hexanes) indicated the reaction was complete. The solvent was then evaporated and the crude was dissolved with DCM and transferred onto a glass column packed with silica gel (~1/2" x 7") and eluted with 5-10% EtOAc/hexanes. Product **6** was isolated as a colourless oil: 92.5 mg, yield = 95%, ee = 92%.

Procedure for the preparation of compound **7**:

A 10 mL flask was charged with [Rh(COD)Cl]₂ (4.3 mg, 0.00872 mmol), (*R*)-(-*S*)- PPF-P(*t*-Bu)₂ ligand **3** (9.4 mg, 0.0173 mmol), oxabicycle **1** (50 mg, 0.347 mmol), and *trans*-1-hexen-1-ylboronic acid (54 mg, 0.422 mmol). A stir bar was added and the flask was sealed and flushed with nitrogen before distilled THF (2 mL) and Cs₂CO₃ (5M) in H₂O (35 µL, 0.175 mmol Cs₂CO₃) were added by syringe. The reaction was stirred for 18 h, after which time ¹H NMR analysis indicated the reaction was complete. The solvent was then evaporated and the crude

was dissolved with DCM and transferred onto a glass column packed with silica gel (~1/2" x 3") and eluted with 4% EtOAc/hexanes. Product **7** was isolated as a colourless oil: 73.4 mg, yield = 93%, ee = 88%.

Procedure for the derivatization of compound **2**:

A 100 mL flask with stir bar containing **2** (0.175 g, 0.786 mmol) was charged with ethanol (8 mL) and THF (2.5 mL). The solution was cooled in an ice bath before hydrazine- H_2O (1.5 mL, 30.9 mmol) was added. A hot saturated solution of NaIO_4 (1.65 g, 7.73 mmol) in water was added dropwise. A water condenser was attached to the flask and the resulting white foam was stirred vigorously in an oil bath at 80°C . After heating for 1 h all the foam had dissipated. The reaction was cooled to room temperature and diluted with DCM and brine solution, mixed well, and separated. The aqueous layer was re-extracted twice with DCM, and the combined organics were dried over MgSO_4 . The crude oil was adsorbed onto a minimum amount of silica gel and transferred onto a column pre-packed with silica gel (~1/2 x 6"). The desired product was eluted with 2-6% EtOAc/hexanes and evaporated down to a flaky white solid: 0.128 g, 73% yield.

Product **13** was derivatized by reacting with 4-bromobenzoyl chloride (2 eq.), NEt_3 (2 eq.) and 4-dimethylaminopyridine (1 eq.) in DCM (unoptimized procedure). Excess 4-bromobenzoyl chloride was hydrolyzed by stirring vigorously the resulting crude solid (after evaporation) in aqueous NaHCO_3 solution for 2 h. The aqueous solution was extracted with DCM, and the resulting mixture was purified by filtering through a plug of silica gel (to remove DMAP) and a plug of neutral aluminium oxide (to remove 4-bromobenzoic acid) and eluting with DCM. The resulting pure white solid **14** was recrystallized from hot CH_3CN to obtain crystals for x-ray analysis.

Table 1. Initial Ligand Screening. Rh-Catalyzed ARO with Activated Phenylboronate^a

Entry	Ligand	Time	Yield % ^b	ee % ^c
1	DPPF	20 min.	71	-
3	BINAP	30 min.	43	16
2	tol-BINAP	30 min.	53	19
4	ⁱ Pr-POX ^d	4 h	n.r.	-
5	PPF-P ^t Bu ₂	20 min.	71	67

^aConditions: 1 mol% [Rh(COD)Cl]₂, 2.5 mol% ligand, 5 eq. phenylboronic acid derivative, ~1.0 M in THF. ^b Isolated yield. ^c Determined by chiral HPLC (Chiracel OD column). ^d ⁱPr-POX = isopropyl diphenylphosphinophenyl oxazoline.

3. Characterization

Absolute and relative configurations of the products in this paper have been assigned by analogy to the structure of compound **14**, determined by x-ray structure determination. Further support for the relative stereochemistries is taken from identical or similar compounds described previously in the literature.⁵

(-)-(1R, 2S)-1,2-Dihydro-2-phenyl-1-naphthol (2): This compound has previously been characterized in racemic form⁵, and an enantioselective synthesis has also been reported.⁶ *Note: Compound is light-sensitive, especially in non-polar solvents like hexane and dichloromethane.*

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 2% isopropanol/hexanes, 1 mL/min, $\lambda = 254$ nm; t_r (major) = 16.9 min., t_r (minor) = 31.6 min.), 92% ee. $[\alpha]_D^{20} = -168$ ($c = 1.00$, 95% EtOH).⁷

Absolute configuration: The absolute configuration of **2** was determined by x-ray crystallography after conversion to protected tetrahydronaphthalene **14**.

(+)-(1R, 2S, 5S, 6S)-5,6-Bis(methoxymethyl)-2-(4-methylphenyl)-cyclohex-3-enol (5a): Purified by flash column chromatography (~3/4" x 7")

silica gel, eluted with 5-20 % EtOAc/hexanes). Yield = 88%. Colourless oil. R_f = 0.46 (50% EtOAc/hexanes); IR (film) ν = 3419, 2892, 1515, 1458, 1448, 1097, 963, 845, 791 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.13 (4H, s), 5.85 (1H, ddd, J = 10.2, 3.6, 3.2 Hz), 5.78 (1H, dm, J = 11.1 Hz), 3.87 (1H, dm, J = 7.0 Hz), 3.63 (1H, d, J = 9 Hz), 3.57 (2H, d, J = 7.1 Hz), 3.50 (2H+1H, d, J = 7.1 Hz), 3.39 (3H, s), 3.36 (3H, s), 2.61 (1H, m), 2.50 (1H, qd, J = 7.4, 1.9 Hz); ^{13}C (75 MHz, CDCl_3) δ 139.5, 136.0, 129.4, 129.2, 129.01, 128.98, 77.4, 73.2, 71.9, 67.8, 59.1, 48.2, 41.8, 36.3, 21.3; HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3$: 276.1725, found 276.1732.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 5% isopropanol/hexanes, 1 mL/min, λ = 254 nm; t_r (major) = 5.7 min., t_r (minor) = 6.7 min.), 95% ee. $[\alpha]_D^{20}$ = +68 (c = 1.31, CHCl_3).

(+)-(1R, 2S, 5S, 6S)-5,6-Bis(methoxymethyl)-2-phenyl-cyclohex-3-enol

(5b): Purified by flash column chromatography (~3/4" x 7" silica gel, eluted with 5-20 % EtOAc/hexanes). Yield = 91%. Colourless oil. R_f = 0.10 (20%

EtOAc/hexanes); IR (film) ν = 3389, 2885, 1490, 1451, 1390, 1192, 1162, 1097, 964, 830, 754, 701 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.28 (2H, m), 7.28-7.18 (3H, m), 5.87 (1H, ddd, J = 10.2, 3.2, 3.0 Hz), 5.81 (1H, dm, J = 9.5 Hz), 3.91 (1H, dm, J = 7.0 Hz), 3.73 (1H, d, J = 9 Hz), 3.58 (2H, d, J = 7.5 Hz), 3.54 (1H, m), 3.51 (2H, d, J = 3.6 Hz), 3.40 (3H, s), 3.37 (3H, s), 2.64 (1H, m), 2.52 (1H, qd, J = 7.5, 2.1 Hz); ^{13}C (100 MHz, CDCl_3) δ 142.7, 129.5, 129.2, 129.1, 128.3, 126.5, 73.2, 71.8, 67.8, 59.2, 59.1, 48.6, 41.8, 36.3; HRMS calcd for $\text{C}_{16}\text{H}_{22}\text{O}_3$: 262.1569, found 262.1562.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 2% isopropanol/hexanes, 1 mL/min, λ = 254 nm; t_r (major) = 10.9 min., t_r (minor) = 8.5 min.), 95% ee. $[\alpha]_D^{20}$ = +76 (c = 1.00, CHCl_3).

(+)-(1R, 2S, 5S, 6S)-5,6-Bis(methoxymethyl)-2-(4-chlorophenyl)-

cyclohex-3-enol (5d): Purified by flash column chromatography (~3/4" x 7" silica gel, eluted with 5-20 % EtOAc/hexanes). Yield = 95%. Colourless

oil. R_f = 0.34 (50% EtOAc/hexanes); IR (film) ν = 3383, 2896, 1489, 1456, 1091, 1014, 811 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.27 (2H, dm, J = 8.4 Hz), 7.16 (2H, dm, J = 8.4 Hz), 5.87

(1H, ddd, $J = 10.2, 3.6, 3.5$ Hz), 5.73 (1H, dd, $J = 10.2, 1.8$ Hz), 4.0 (1H, d, $J = 9.9$ Hz), 3.84 (1H, dm, $J = 10.8$ Hz) 3.55 (2H, d, $J = 9.0$ Hz), 3.48 (2H+1H, d, $J = 3.0$ Hz), 3.39 (3H, s), 3.36 (3H, s), 2.62 (1H, m), 2.52 (1H, qd, $J = 7.4, 1.8$ Hz); ^{13}C (75 MHz, CDCl_3) δ 141.3, 132.2, 130.6 129.8, 128.8, 128.3, 73.2, 71.8, 67.8, 59.2, 59.1, 48.6, 41.8, 36.3; HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{Cl}$: 296.1179, found 296.1181.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 5% isopropanol/hexanes, 1 mL/min, $\lambda = 220$ nm; t_r (major) = 6.2 min., t_r (minor) = 7.5 min.), 95% ee. $[\alpha]_{\text{D}}^{20} = +59$ ($c = 1.00$, CHCl_3).

(+)-(1R, 2S, 5S, 6S)-5,6-Bis(methoxymethyl)-2-(3-chlorophenyl)-

cyclohex-3-enol (5e): Purified by flash column chromatography (~3/4" x 7" silica gel, eluted with 5-20 % EtOAc/hexanes). Yield = 73%. Colourless

oil. $R_f = 0.34$ (50% EtOAc/hexanes);

IR (film) $\nu = 3374, 2895, 1597, 1477, 1459, 1199, 1168, 1097, 999, 899, 833, 781, 701$ cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.25-7.16 (3H, m), 7.15-7.08 (1H, m), 5.87 (1H, ddd, $J = 9.9, 3.5, 3.3$ Hz), 5.73 (1H, dm, $J = 10.3$ Hz), 4.0 (1H, d, $J = 9.6$ Hz), 3.87 (1H, dm, $J = 9.6$ Hz) 3.56 (2H, d, $J = 7.5$ Hz), 3.49 (2H+1H, d, $J = 3.3$ Hz), 3.40 (3H, s), 3.37 (3H, s), 2.63 (1H, m), 2.52 (1H, qd, $J = 7.5, 2.1$ Hz); ^{13}C (75 MHz, CDCl_3) δ 144.8, 134.0, 129.9, 129.4, 128.5, 127.4, 126.7, 73.0, 71.5, 67.4, 59.20, 59.15, 48.4, 41.7, 36.2; HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Cl}$: 295.1101, found 295.1097.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 5% isopropanol/hexanes, 1 mL/min, $\lambda = 220$ nm; t_r (major) = 6.7 min., t_r (minor) = 3.2 min.), 99% ee. $[\alpha]_{\text{D}}^{20} = +59$ ($c = 1.02$, CHCl_3).

(+)-(1R, 2S, 5S, 6S)-5,6-Bis(methoxymethyl)-2-(3-iodophenyl)-cyclohex-

3-enol (5g): Purified by flash column chromatography (~3/4" x 7" silica gel, eluted with 5-20 % EtOAc/hexanes). Yield = 85%. Colourless oil. $R_f =$

0.43 (50% EtOAc/hexanes); IR (film) $\nu = 3385, 2891, 1589, 1560, 1472, 1421, 1097, 1074, 990, 831, 776$ cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.64-7.51 (2H, m), 7.20 (1H, d, $J = 7.5$ Hz), 7.04 (1H, d, $J = 8.1$ Hz) 5.85 (1H, ddd, $J = 10.2, 3.3, 3.3$ Hz), 5.73 (1H, dm, $J = 9.9$ Hz), 3.97

(1H, d, $J = 9.9$ Hz), 3.87 (1H, dm, $J = 9.6$ Hz) 3.56 (2H, d, $J = 7.5$ Hz), 3.49 (2H, d, $J = 3.0$ Hz), 3.45 (1H, m), 3.40 (3H, s), 3.37 (3H, s), 2.62 (1H, m), 2.52 (1H, qd, $J = 7.5, 1.8$ Hz); ^{13}C (75 MHz, CDCl_3) δ 145.3, 138.2, 135.5, 129.94, 129.91, 128.6, 128.5, 94.5, 73.0, 71.5, 67.4, 59.21, 59.16, 48.3, 41.7, 36.2; HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{IO}_3$: 388.0535, found 388.0536.

Assay of enantiomeric excess: chiral HPLC (Chiracel AD, 2% isopropanol/hexanes, 1 mL/min, $\lambda = 220$ nm; t_r (major) = 10.7 min., t_r (minor) = 15.0 min.), 95% ee. $[\alpha]_{\text{D}}^{20} = +49$ ($c = 1.00$, CHCl_3).

(+)-(1R, 2S, 5S, 6S)-5,6-Bis(methoxymethyl)-2-(4-acetylphenyl)-

cyclohex-3-enol (5g): Purified by flash column chromatography (~3/4" x 7" silica gel, eluted with 10-40 % EtOAc/hexanes). Yield = 85%.

Colourless oil. $R_f = 0.31$ (50% EtOAc/hexanes); IR (film) $\nu = 3382, 2895, 1670, 1607, 1359, 1271, 1096, 959, 813$ cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.91 (2H, d, $J = 8.1$ Hz), 7.33 (2H, d, $J = 8.4$ Hz), 5.88 (1H, ddd, $J = 10.2, 3.3, 3.3$ Hz), 5.78 (1H, dd, $J = 10.2, 1.8$ Hz), 4.14 (1H, d, $J = 9.9$ Hz), 3.90 (1H, dm, $J = 9.9$ Hz) 3.56 (2H+1H, d, $J = 7.5$ Hz), 3.50 (2H, d, $J = 3.0$ Hz), 3.40 (3H, s), 3.37 (3H, s), 2.64 (1H, m), 2.60-2.49 (3H+1H, m); ^{13}C (75 MHz, CDCl_3) δ 198.0, 148.4, 135.3, 129.7, 129.2, 128.2, 128.1, 72.7, 71.1, 67.1, 58.93, 58.90, 48.4, 41.5, 36.0, 26.6; HRMS calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$: 304.1675, found 304.1669.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 10% isopropanol/hexanes, 1 mL/min, $\lambda = 220$ nm; t_r (major) = 11.1 min., t_r (minor) = 14.4 min.), 94% ee. $[\alpha]_{\text{D}}^{20} = +47$ ($c = 1.03$, CHCl_3).

(+)-(1R, 2S, 5S, 6S)-5,6-Bis(methoxymethyl)-2-(4-methoxyphenyl)-

cyclohex-3-enol (5i): Purified by flash column chromatography (~3/4" x 7" silica gel, eluted with 5-20 % EtOAc/hexanes). Yield = 87%.

Colourless oil. $R_f = 0.34$ (50% EtOAc/hexanes);

IR (film) $\nu = 3399, 2892, 1610, 1512, 1458, 1245, 1176, 1097, 1030, 815, 798$ cm^{-1} ;

^1H NMR (300 MHz, CDCl_3) δ 7.15 (2H, dm, $J = 8.6$ Hz), 6.86 (2H, dm, $J = 8.6$ Hz), 5.85 (1H, ddd, $J = 10.3, 3.4, 3.4$ Hz), 5.76 (1H, dm, $J = 10.2$ Hz), 3.86 (1H, dm, $J = 9.9$ Hz), 3.78 (3H, s), 3.70 (1H, d, $J = 9.0$ Hz), 3.56 (2H, d, $J = 7.4$ Hz), 3.49 (2H+1H, d, $J = 3.4$ Hz), 3.39 (3H, s),

3.36 (3H, s), 2.61 (1H, m), 2.50 (1H, qd, $J = 7.5, 2.1$ Hz); ^{13}C (75 MHz, CDCl_3) δ 158.1, 134.5, 129.8, 129.14, 129.10, 113.5, 72.9, 71.6, 67.6, 58.9, 55.2, 47.5, 41.5, 36.0; HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: 292.1675, found 292.1677.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 10% isopropanol/hexanes, 1 mL/min, $\lambda = 220$ nm; t_r (major) = 6.6 min., t_r (minor) = 9.5 min.), 96% ee. $[\alpha]_D^{20} = +50$ ($c = 1.14$, CHCl_3).

(+)-(1*R*, 2*S*, 5*S*, 6*S*)-5,6-Bis(methoxymethyl)-2-(3-methoxyphenyl)-cyclohex-3-enol (5j): Purified by flash column chromatography (~3/4" x 7" silica gel, eluted with 5-20 % EtOAc/hexanes). Yield = 91%.

Colourless oil. $R_f = 0.34$ (50% EtOAc/hexanes);

IR (film) $\nu = 3379, 2886, 2837, 1599, 1585, 1487, 1459, 1286, 1265, 1198, 1167, 1093, 1054, 998, 777, 699$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (1H, t, $J = 7.9$ Hz), 6.86-6.70 (3H, m), 5.85 (1H, dm, $J = 10.3$), 5.79 (1H, dm, $J = 10.3$ Hz), 3.91 (1H, dm, $J = 8.0$ Hz), 3.78 (3H, s), 3.66 (1H, d, $J = 9.2$ Hz), 3.56 (2H, d, $J = 7.5$ Hz), 3.52-3.42 (2H+1H, d, $J = 3.5$ Hz), 3.39 (3H, s), 3.37 (3H, s), 2.61 (1H, m), 2.50 (1H, qd, $J = 7.5, 2.1$ Hz); ^{13}C (100 MHz, CDCl_3) δ 159.6, 144.2, 129.5, 129.1, 128.8, 121.5, 114.9, 111.8, 76.9, 73.1, 71.8, 67.7, 59.1, 55.3, 48.5, 41.7, 36.2; HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: 292.1675, found 292.1674.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 5% isopropanol/hexanes, 1 mL/min, $\lambda = 254$ nm; t_r (major) = 9.2 min., t_r (minor) = 15.7 min.), 95% ee. $[\alpha]_D^{20} = +70$ ($c = 1.00$, CHCl_3).

(+)-(1*R*, 2*R*, 5*S*, 6*S*)-5,6-Bis(*p*-methoxybenzyloxymethyl)-2-(1-(*E*)-hexenyl)-cyclohex-3-enol (6): Purified by flash column chromatography (~1/2" x 7" silica gel, eluted with 5-10 %

EtOAc/hexanes). Yield = 95%. Colourless oil. $R_f = 0.27$ (20% EtOAc/hexanes); IR (film) $\nu = 3406, 2924, 2855, 1611, 1585, 1512, 1467, 1364, 1299, 1246, 1170, 1070, 1032, 971, 819, 758$ cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.22 (4H, tm, $J = 8.7$ Hz), 6.91-6.83 (4H, m), 5.69-5.45 (4H, m), 4.48 (1H, d, $J = 12.0$ Hz), 4.34 (2H, d, $J = 11.7$ Hz), 4.23 (1H, d, $J = 11.4$ Hz), 3.87 (1H, d, $J = 9.6$ Hz), 3.80 (6H, s), 3.77 (1H, m), 3.58-3.36 (4H, m), 2.80 (1H, m), 2.55 (1H, m),

2.35 (1H, qm, $J = 7.8$ Hz), 2.05 (2H, q, $J = 6.9$ Hz), 1.42-1.20 (4H, m), 0.89 (3H, t, $J = 7.2$ Hz); ^{13}C (75 MHz, CDCl_3) δ 159.6, 159.4, 132.1, 131.0, 130.7, 130.1, 129.7, 129.6, 129.5, 128.3, 114.04, 113.98, 76.8, 73.11, 73.08, 70.5, 68.4, 67.9, 55.5, 45.8, 41.6, 36.2, 32.6, 31.9, 22.5, 14.2; HRMS calcd for $\text{C}_{30}\text{H}_{40}\text{O}_5$: 480.2876, found 480.2864.

Assay of enantiomeric excess: chiral HPLC (Chiracel AD, 5% isopropanol/hexanes, 1 mL/min, $\lambda = 254$ nm; t_r (major) = 13.2 min., t_r (minor) = 10.7 min.), 92% ee. $[\alpha]_{\text{D}}^{20} = +26$ ($c = 1.14$, CHCl_3).

(-)-(1R, 2R)-1,2-Dihydro-2-(1-(E)-hexenyl)-1-naphthol (7): Purified by

flash column chromatography ($\sim 1/2'' \times 3''$ silica gel, eluted with 4%

EtOAc/hexanes). Yield = 93%. Colourless oil. $R_f = 0.45$ (25%

EtOAc/hexanes); IR (film) $\nu = 3423, 3032, 2956, 2926, 2856, 1483, 1452, 1378, 1187, 1050, 971, 786, 764, 695, 660 \text{ cm}^{-1}$; ^1H NMR (300 MHz, CDCl_3) δ 7.50-7.39 (1H, m), 7.32-7.18 (2H, m), 7.12-7.02 (1H, m), 6.49 (1H, dd, $J = 9.6, 1.2$ Hz), 5.94 (1H, dd, $J = 9.5, 4.8$ Hz), 5.73 (1H, dt, $J = 15.6, 6.6$ Hz), 5.34 (1H, dd, $J = 15.3, 8.7$ Hz), 4.80 (1H, dd, $J = 8.6, 5.7$ Hz), 3.13 (1H, m), 2.05 (2H, dt, $J = 6.9, 6.9$ Hz), 1.80 (1H, d, $J = 8.4$ Hz) 1.42-1.20 (4H, m), 0.89 (3H, t, $J = 7.2$ Hz); ^{13}C (100 MHz, CDCl_3) δ 137.4, 136.6, 132.9, 130.0, 128.1, 128.0, 127.4, 126.5, 126.2, 125.8; HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: 228.1514, found 228.1513.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 2% isopropanol/hexanes, 1 mL/min, $\lambda = 254$ nm; t_r (major) = 7.8 min., t_r (minor) = 9.5 min.), 88% ee. $[\alpha]_{\text{D}}^{20} = -259$ ($c = 0.64$, CHCl_3).

(-)-(1R, 2S)-6,7-Difluoro-1,2-dihydro-2-phenyl-1-naphthol (10a): *Note:*

Compound is light-sensitive, especially in non-polar solvents like hexane

and dichloromethane. Purified by flash column chromatography ($\sim 1/2'' \times 7''$

silica gel, eluted with 2-10% EtOAc/hexanes. Crude material was adsorbed onto a minimum of silica gel and transferred onto column). Yield = 60%. Pale yellow oil. $R_f = 0.27$ (25%

EtOAc/hexanes); IR (film) $\nu = 3379, 3401, 1594, 1508, 1377, 1308, 1108, 1067, 881, 777, 760, 702 \text{ cm}^{-1}$; ^1H NMR (300 MHz, CD_3OD) δ 7.27-7.13 (6H, m), 7.09 (1H, dd, $J = 11.1, 7.8$ Hz), 6.63 (1H, dd, $J = 9.6, 1.8$ Hz), 6.15 (1H, dd, $J = 9.6, 4.5$ Hz), 4.89 (1H, d, $J = 6.3$ Hz),

3.76 (1H, m); ^{13}C (75.5 MHz, CD_3OD) δ 151.1 (dd, $J^{C-F} = 245, 12.9$ Hz), 150.9 (dd, $J^{C-F} = 247, 12.6$ Hz), 139.4, 135.7 (m), 132.71, 132.68, 131.8 (m), 130.7, 129.3, 128.1, 127.3, 116.8 (d, $J^{C-F} = 18.6$ Hz), 115.9 (d, $J^{C-F} = 18.0$ Hz), 71.4, 48.2; ^{19}F NMR (282.3 MHz, CD_3OD) δ -133.9 (ddd, $J = 20.6, 10.7, 8.5$ Hz), -140.1 (ddd, $J = 20.0, 10.4, 8.2$ Hz); HRMS calcd for $\text{C}_{16}\text{H}_{12}\text{F}_2\text{O}$: 258.0856, found 258.0857.

Assay of enantiomeric excess: chiral HPLC (Chiracel OD, 5% isopropanol/hexanes, 1 mL/min, $\lambda = 254$ nm; t_r (major) = 10.5 min., t_r (minor) = 18.8 min.), 91% ee. $[\alpha]_D^{20} = -163$ (c = 0.64, MeOH).

4. X-ray data for compound **14**:

Figure 1. X-ray crystal structure of **14** (conformer A).

Figure 2. X-ray crystal structure of **14** (conformer B).

Figure 3. X-ray crystal structure of **14** (conformer C)

Figure 4. X-ray crystal structure of **14** (conformer D).

Table 2. Crystal data and structure refinement for **14**.

Identification code	k0204	
Empirical formula	C ₂₃ H ₁₉ Br O ₂	
Formula weight	407.29	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 6.05380(10) Å	α = 116.3490(10)°.
	b = 17.6308(2) Å	β = 92.5730(10)°.
	c = 19.3609(3) Å	γ = 93.8090(10)°.
Volume	1841.27(5) Å ³	
Z	4	
Density (calculated)	1.469 Mg/m ³	
Absorption coefficient	2.247 mm ⁻¹	
F(000)	832	
Crystal size	0.30 x 0.10 x 0.10 mm ³	
Theta range for data collection	2.59 to 27.42°.	
Index ranges	-7 ≤ h ≤ 7, -22 ≤ k ≤ 22, -24 ≤ l ≤ 24	
Reflections collected	24177	
Independent reflections	15135 [R(int) = 0.074]	
Completeness to theta = 27.42°	99.2 %	
Absorption correction	None	
Max. and min. transmission	0.8065 and 0.5522	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	15135 / 3 / 938	
Goodness-of-fit on F ²	0.992	
Final R indices [I > 2σ(I)]	R1 = 0.0460, wR2 = 0.0868	
R indices (all data)	R1 = 0.0760, wR2 = 0.0999	
Absolute structure parameter	0.002(5)	
Extinction coefficient	0.0065(5)	
Largest diff. peak and hole	0.473 and -0.439 e.Å ⁻³	

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Br(1A)	2804(1)	3590(1)	6896(1)	45(1)
O(1A)	5535(4)	5709(2)	4807(2)	24(1)
O(2A)	8924(5)	5319(2)	4957(2)	35(1)
C(1A)	6397(7)	6108(3)	4334(2)	26(1)
C(2A)	6092(8)	5459(3)	3492(3)	31(1)
C(3A)	7665(8)	4868(3)	3191(3)	35(1)
C(4A)	7422(10)	4266(3)	2418(3)	49(1)
C(5A)	5613(10)	4255(4)	1948(3)	53(2)
C(6A)	4077(9)	4838(4)	2240(3)	44(1)
C(7A)	4309(8)	5447(3)	3012(3)	36(1)
C(8A)	2626(8)	6102(3)	3298(3)	36(1)
C(9A)	2699(7)	6571(3)	4173(3)	33(1)
C(10A)	5119(7)	6879(3)	4512(3)	28(1)
C(11A)	6985(7)	5336(3)	5073(2)	26(1)
C(12A)	5902(7)	4938(3)	5526(2)	26(1)
C(13A)	7062(8)	4364(3)	5674(3)	33(1)
C(14A)	6158(8)	3964(3)	6081(3)	41(1)
C(15A)	4110(8)	4162(3)	6369(3)	33(1)
C(16A)	2959(8)	4749(3)	6246(3)	33(1)
C(17A)	3847(8)	5122(3)	5810(3)	32(1)
C(18A)	5397(7)	7533(3)	5353(3)	28(1)
C(19A)	7323(7)	8074(3)	5624(3)	30(1)
C(20A)	7635(9)	8720(3)	6378(3)	39(1)
C(21A)	5979(9)	8815(3)	6876(3)	38(1)
C(22A)	4076(9)	8265(3)	6618(3)	35(1)
C(23A)	3766(7)	7619(3)	5865(3)	31(1)
Br(1B)	8369(1)	12142(1)	7052(1)	45(1)
O(1B)	10432(4)	9832(2)	8987(2)	27(1)
O(2B)	13825(5)	9851(2)	8557(2)	44(1)
C(1B)	11195(7)	9462(3)	9498(2)	26(1)
C(2B)	11050(7)	10121(3)	10313(2)	26(1)

C(3B)	12733(8)	10778(3)	10656(3)	37(1)
C(4B)	12680(9)	11407(3)	11402(3)	45(1)
C(5B)	10885(10)	11377(4)	11818(3)	48(1)
C(6B)	9217(8)	10723(3)	11484(3)	40(1)
C(7B)	9244(8)	10082(3)	10725(3)	31(1)
C(8B)	7416(7)	9364(3)	10387(3)	31(1)
C(9B)	7366(7)	8861(3)	9511(3)	29(1)
C(10B)	9704(7)	8644(3)	9278(3)	25(1)
C(11B)	11905(7)	10018(3)	8582(2)	27(1)
C(12B)	10951(7)	10483(3)	8175(2)	23(1)
C(13B)	12116(7)	10582(3)	7609(3)	29(1)
C(14B)	11331(8)	11055(3)	7254(3)	32(1)
C(15B)	9407(7)	11437(3)	7485(3)	30(1)
C(16B)	8241(8)	11354(3)	8048(3)	34(1)
C(17B)	9005(8)	10863(3)	8387(3)	33(1)
C(18B)	9834(7)	7997(3)	8448(3)	26(1)
C(19B)	11654(7)	7522(3)	8245(3)	33(1)
C(20B)	11802(8)	6899(3)	7500(3)	37(1)
C(21B)	10131(8)	6743(3)	6932(3)	35(1)
C(22B)	8334(8)	7215(3)	7113(3)	34(1)
C(23B)	8169(7)	7838(3)	7869(3)	31(1)
Br(1C)	14845(1)	8516(1)	3572(1)	45(1)
O(1C)	16758(5)	4939(2)	368(2)	27(1)
O(2C)	20276(5)	5361(2)	907(2)	40(1)
C(1C)	17503(7)	4187(3)	-274(2)	26(1)
C(2C)	17440(7)	3456(3)	-55(3)	28(1)
C(3C)	19242(8)	3391(3)	381(3)	33(1)
C(4C)	19225(9)	2734(3)	587(3)	38(1)
C(5C)	17387(10)	2138(3)	361(3)	43(1)
C(6C)	15620(9)	2199(3)	-76(3)	40(1)
C(7C)	15612(7)	2846(3)	-303(3)	32(1)
C(8C)	13683(8)	2858(3)	-816(3)	34(1)
C(9C)	13596(7)	3701(3)	-860(3)	31(1)
C(10C)	15924(7)	4003(3)	-979(2)	29(1)
C(11C)	18310(7)	5463(3)	911(3)	26(1)
C(12C)	17405(7)	6204(3)	1534(2)	26(1)

C(13C)	18723(8)	6667(3)	2207(3)	32(1)
C(14C)	18017(8)	7363(3)	2820(3)	33(1)
C(15C)	15903(7)	7597(3)	2729(3)	30(1)
C(16C)	14548(8)	7150(3)	2049(3)	33(1)
C(17C)	15285(7)	6451(3)	1452(3)	30(1)
C(18C)	16032(8)	4732(3)	-1197(3)	31(1)
C(19C)	17760(8)	4826(3)	-1606(3)	39(1)
C(20C)	17908(10)	5467(4)	-1832(3)	49(1)
C(21C)	16283(10)	6020(4)	-1654(3)	51(2)
C(22C)	14529(10)	5939(3)	-1244(3)	48(1)
C(23C)	14437(9)	5305(3)	-1010(3)	40(1)
Br(1D)	9354(1)	6994(1)	136(1)	45(1)
O(1D)	12575(5)	10627(2)	3441(2)	25(1)
O(2D)	15926(5)	10329(2)	2968(2)	39(1)
C(1D)	13600(7)	11399(3)	4098(2)	26(1)
C(2D)	13520(7)	12147(3)	3903(2)	29(1)
C(3D)	15180(8)	12273(3)	3467(3)	34(1)
C(4D)	15123(10)	12944(3)	3280(3)	46(1)
C(5D)	13458(10)	13484(3)	3514(3)	45(1)
C(6D)	11869(9)	13363(3)	3951(3)	41(1)
C(7D)	11864(7)	12697(3)	4158(3)	31(1)
C(8D)	9973(7)	11744(3)	4669(3)	28(1)
C(8E)	10168(8)	12614(3)	4674(3)	34(1)
C(10D)	12290(7)	11512(3)	4789(2)	24(1)
C(11D)	13930(7)	10156(3)	2917(3)	28(1)
C(12D)	12733(7)	9399(3)	2272(2)	25(1)
C(13D)	13872(7)	8964(3)	1622(3)	33(1)
C(14D)	12910(8)	8246(3)	989(3)	33(1)
C(15D)	10737(8)	7956(3)	1008(2)	29(1)
C(16D)	9559(7)	8367(3)	1648(3)	30(1)
C(17D)	10540(7)	9096(3)	2270(3)	28(1)
C(18D)	12367(7)	10759(3)	4967(2)	27(1)
C(19D)	14279(8)	10664(3)	5332(3)	36(1)
C(20D)	14367(9)	10000(3)	5529(3)	42(1)
C(21D)	12546(10)	9416(3)	5357(3)	47(1)
C(22D)	10650(10)	9489(3)	4982(3)	47(1)

C(23D)	10554(8)	10159(3)	4789(3)	34(1)
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Table 4. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **14**.

Br(1A)-C(15A)	1.887(4)
O(1A)-C(11A)	1.343(4)
O(1A)-C(1A)	1.473(5)
O(2A)-C(11A)	1.205(5)
C(1A)-C(2A)	1.513(6)
C(1A)-C(10A)	1.520(6)
C(2A)-C(7A)	1.386(6)
C(2A)-C(3A)	1.406(7)
C(3A)-C(4A)	1.391(7)
C(4A)-C(5A)	1.386(8)
C(5A)-C(6A)	1.378(8)
C(6A)-C(7A)	1.393(7)
C(7A)-C(8A)	1.522(7)
C(8A)-C(9A)	1.517(7)
C(9A)-C(10A)	1.537(6)
C(10A)-C(18A)	1.514(6)
C(11A)-C(12A)	1.493(6)
C(12A)-C(17A)	1.383(6)
C(12A)-C(13A)	1.392(5)
C(13A)-C(14A)	1.377(6)
C(14A)-C(15A)	1.384(7)
C(15A)-C(16A)	1.383(6)
C(16A)-C(17A)	1.386(6)
C(18A)-C(19A)	1.377(6)
C(18A)-C(23A)	1.398(6)
C(19A)-C(20A)	1.391(7)
C(20A)-C(21A)	1.388(7)
C(21A)-C(22A)	1.373(7)
C(22A)-C(23A)	1.390(7)
Br(1B)-C(15B)	1.903(4)
O(1B)-C(11B)	1.331(5)
O(1B)-C(1B)	1.481(4)
O(2B)-C(11B)	1.216(5)
C(1B)-C(2B)	1.498(6)

C(1B)-C(10B)	1.524(6)
C(2B)-C(3B)	1.385(7)
C(2B)-C(7B)	1.397(6)
C(3B)-C(4B)	1.380(7)
C(4B)-C(5B)	1.393(8)
C(5B)-C(6B)	1.375(8)
C(6B)-C(7B)	1.403(7)
C(7B)-C(8B)	1.506(7)
C(8B)-C(9B)	1.524(6)
C(9B)-C(10B)	1.526(6)
C(10B)-C(18B)	1.511(6)
C(11B)-C(12B)	1.490(5)
C(12B)-C(17B)	1.381(6)
C(12B)-C(13B)	1.398(6)
C(13B)-C(14B)	1.387(6)
C(14B)-C(15B)	1.376(6)
C(15B)-C(16B)	1.381(6)
C(16B)-C(17B)	1.386(6)
C(18B)-C(23B)	1.391(6)
C(18B)-C(19B)	1.392(6)
C(19B)-C(20B)	1.384(7)
C(20B)-C(21B)	1.379(6)
C(21B)-C(22B)	1.377(6)
C(22B)-C(23B)	1.399(7)
Br(1C)-C(15C)	1.893(4)
O(1C)-C(11C)	1.333(5)
O(1C)-C(1C)	1.474(5)
O(2C)-C(11C)	1.216(5)
C(1C)-C(2C)	1.525(6)
C(1C)-C(10C)	1.526(6)
C(2C)-C(3C)	1.391(6)
C(2C)-C(7C)	1.395(6)
C(3C)-C(4C)	1.384(6)
C(4C)-C(5C)	1.388(7)
C(5C)-C(6C)	1.374(7)
C(6C)-C(7C)	1.394(6)

C(7C)-C(8C)	1.505(6)
C(8C)-C(9C)	1.532(6)
C(9C)-C(10C)	1.536(6)
C(10C)-C(18C)	1.518(6)
C(11C)-C(12C)	1.489(6)
C(12C)-C(13C)	1.370(6)
C(12C)-C(17C)	1.406(6)
C(13C)-C(14C)	1.386(7)
C(14C)-C(15C)	1.397(6)
C(15C)-C(16C)	1.387(6)
C(16C)-C(17C)	1.382(6)
C(18C)-C(23C)	1.387(7)
C(18C)-C(19C)	1.385(7)
C(19C)-C(20C)	1.381(7)
C(20C)-C(21C)	1.377(8)
C(21C)-C(22C)	1.390(8)
C(22C)-C(23C)	1.378(7)
Br(1D)-C(15D)	1.889(5)
O(1D)-C(11D)	1.345(5)
O(1D)-C(1D)	1.461(5)
O(2D)-C(11D)	1.215(5)
C(1D)-C(2D)	1.527(6)
C(1D)-C(10D)	1.529(6)
C(2D)-C(7D)	1.392(6)
C(2D)-C(3D)	1.409(6)
C(3D)-C(4D)	1.385(6)
C(4D)-C(5D)	1.383(8)
C(5D)-C(6D)	1.375(7)
C(6D)-C(7D)	1.401(6)
C(7D)-C(8E)	1.508(7)
C(8D)-C(10D)	1.523(6)
C(8D)-C(8E)	1.526(6)
C(10D)-C(18D)	1.516(6)
C(11D)-C(12D)	1.476(6)
C(12D)-C(13D)	1.392(6)
C(12D)-C(17D)	1.397(6)

C(13D)-C(14D)	1.381(7)
C(14D)-C(15D)	1.387(6)
C(15D)-C(16D)	1.385(6)
C(16D)-C(17D)	1.384(6)
C(18D)-C(19D)	1.387(6)
C(18D)-C(23D)	1.389(6)
C(19D)-C(20D)	1.386(6)
C(20D)-C(21D)	1.378(8)
C(21D)-C(22D)	1.374(8)
C(22D)-C(23D)	1.393(6)

C(11A)-O(1A)-C(1A)	117.0(3)
O(1A)-C(1A)-C(2A)	108.7(3)
O(1A)-C(1A)-C(10A)	106.4(3)
C(2A)-C(1A)-C(10A)	113.3(3)
C(7A)-C(2A)-C(3A)	119.5(4)
C(7A)-C(2A)-C(1A)	121.1(4)
C(3A)-C(2A)-C(1A)	119.3(4)
C(4A)-C(3A)-C(2A)	120.4(5)
C(5A)-C(4A)-C(3A)	119.4(5)
C(6A)-C(5A)-C(4A)	120.3(5)
C(5A)-C(6A)-C(7A)	120.9(5)
C(2A)-C(7A)-C(6A)	119.5(5)
C(2A)-C(7A)-C(8A)	121.6(4)
C(6A)-C(7A)-C(8A)	118.9(4)
C(9A)-C(8A)-C(7A)	113.2(3)
C(8A)-C(9A)-C(10A)	109.6(4)
C(18A)-C(10A)-C(1A)	114.1(3)
C(18A)-C(10A)-C(9A)	115.0(4)
C(1A)-C(10A)-C(9A)	108.8(4)
O(2A)-C(11A)-O(1A)	124.3(4)
O(2A)-C(11A)-C(12A)	123.9(3)
O(1A)-C(11A)-C(12A)	111.9(3)
C(17A)-C(12A)-C(13A)	119.1(4)
C(17A)-C(12A)-C(11A)	123.4(3)
C(13A)-C(12A)-C(11A)	117.4(4)

C(14A)-C(13A)-C(12A)	120.7(4)
C(13A)-C(14A)-C(15A)	119.4(4)
C(16A)-C(15A)-C(14A)	120.8(4)
C(16A)-C(15A)-Br(1A)	119.3(4)
C(14A)-C(15A)-Br(1A)	119.8(3)
C(15A)-C(16A)-C(17A)	119.2(4)
C(12A)-C(17A)-C(16A)	120.7(4)
C(19A)-C(18A)-C(23A)	118.5(4)
C(19A)-C(18A)-C(10A)	118.8(4)
C(23A)-C(18A)-C(10A)	122.7(4)
C(18A)-C(19A)-C(20A)	121.8(4)
C(21A)-C(20A)-C(19A)	119.2(5)
C(22A)-C(21A)-C(20A)	119.5(5)
C(21A)-C(22A)-C(23A)	121.2(4)
C(22A)-C(23A)-C(18A)	119.7(4)
C(11B)-O(1B)-C(1B)	118.7(3)
O(1B)-C(1B)-C(2B)	106.8(3)
O(1B)-C(1B)-C(10B)	107.1(3)
C(2B)-C(1B)-C(10B)	113.7(3)
C(3B)-C(2B)-C(7B)	120.0(4)
C(3B)-C(2B)-C(1B)	119.1(4)
C(7B)-C(2B)-C(1B)	120.9(4)
C(4B)-C(3B)-C(2B)	121.7(5)
C(3B)-C(4B)-C(5B)	118.9(5)
C(6B)-C(5B)-C(4B)	119.8(5)
C(5B)-C(6B)-C(7B)	121.9(5)
C(2B)-C(7B)-C(6B)	117.7(5)
C(2B)-C(7B)-C(8B)	122.0(4)
C(6B)-C(7B)-C(8B)	120.3(4)
C(7B)-C(8B)-C(9B)	113.1(4)
C(8B)-C(9B)-C(10B)	109.8(4)
C(18B)-C(10B)-C(1B)	112.8(3)
C(18B)-C(10B)-C(9B)	115.3(4)
C(1B)-C(10B)-C(9B)	109.4(3)
O(2B)-C(11B)-O(1B)	124.5(4)
O(2B)-C(11B)-C(12B)	123.3(4)

O(1B)-C(11B)-C(12B)	112.1(3)
C(17B)-C(12B)-C(13B)	119.7(4)
C(17B)-C(12B)-C(11B)	120.7(4)
C(13B)-C(12B)-C(11B)	119.4(4)
C(14B)-C(13B)-C(12B)	120.6(4)
C(15B)-C(14B)-C(13B)	118.4(4)
C(14B)-C(15B)-C(16B)	121.9(4)
C(14B)-C(15B)-Br(1B)	119.6(3)
C(16B)-C(15B)-Br(1B)	118.5(3)
C(15B)-C(16B)-C(17B)	119.4(4)
C(12B)-C(17B)-C(16B)	119.9(4)
C(23B)-C(18B)-C(19B)	117.7(4)
C(23B)-C(18B)-C(10B)	122.6(4)
C(19B)-C(18B)-C(10B)	119.8(4)
C(20B)-C(19B)-C(18B)	121.8(4)
C(21B)-C(20B)-C(19B)	119.9(4)
C(22B)-C(21B)-C(20B)	119.5(5)
C(21B)-C(22B)-C(23B)	120.6(4)
C(18B)-C(23B)-C(22B)	120.5(4)
C(11C)-O(1C)-C(1C)	117.1(3)
O(1C)-C(1C)-C(2C)	108.8(3)
O(1C)-C(1C)-C(10C)	105.8(3)
C(2C)-C(1C)-C(10C)	113.0(4)
C(3C)-C(2C)-C(7C)	120.3(4)
C(3C)-C(2C)-C(1C)	119.4(4)
C(7C)-C(2C)-C(1C)	120.3(4)
C(4C)-C(3C)-C(2C)	120.5(5)
C(3C)-C(4C)-C(5C)	119.6(4)
C(6C)-C(5C)-C(4C)	119.7(4)
C(5C)-C(6C)-C(7C)	121.8(5)
C(6C)-C(7C)-C(2C)	118.0(4)
C(6C)-C(7C)-C(8C)	119.6(4)
C(2C)-C(7C)-C(8C)	122.3(4)
C(7C)-C(8C)-C(9C)	114.1(4)
C(8C)-C(9C)-C(10C)	109.3(3)
C(18C)-C(10C)-C(1C)	112.4(4)

C(18C)-C(10C)-C(9C)	115.6(3)
C(1C)-C(10C)-C(9C)	109.4(3)
O(2C)-C(11C)-O(1C)	124.3(4)
O(2C)-C(11C)-C(12C)	122.4(4)
O(1C)-C(11C)-C(12C)	113.3(3)
C(13C)-C(12C)-C(17C)	119.2(4)
C(13C)-C(12C)-C(11C)	118.0(4)
C(17C)-C(12C)-C(11C)	122.7(4)
C(12C)-C(13C)-C(14C)	122.1(4)
C(13C)-C(14C)-C(15C)	117.8(4)
C(16C)-C(15C)-C(14C)	121.4(4)
C(16C)-C(15C)-Br(1C)	119.8(3)
C(14C)-C(15C)-Br(1C)	118.7(3)
C(17C)-C(16C)-C(15C)	119.4(4)
C(16C)-C(17C)-C(12C)	120.0(4)
C(23C)-C(18C)-C(19C)	118.2(4)
C(23C)-C(18C)-C(10C)	122.4(4)
C(19C)-C(18C)-C(10C)	119.4(4)
C(20C)-C(19C)-C(18C)	121.6(5)
C(21C)-C(20C)-C(19C)	119.2(5)
C(20C)-C(21C)-C(22C)	120.4(5)
C(23C)-C(22C)-C(21C)	119.5(5)
C(22C)-C(23C)-C(18C)	121.0(5)
C(11D)-O(1D)-C(1D)	116.9(3)
O(1D)-C(1D)-C(2D)	109.1(3)
O(1D)-C(1D)-C(10D)	106.4(3)
C(2D)-C(1D)-C(10D)	112.5(3)
C(7D)-C(2D)-C(3D)	120.9(4)
C(7D)-C(2D)-C(1D)	120.8(4)
C(3D)-C(2D)-C(1D)	118.4(4)
C(4D)-C(3D)-C(2D)	119.1(5)
C(5D)-C(4D)-C(3D)	120.7(5)
C(6D)-C(5D)-C(4D)	119.6(5)
C(5D)-C(6D)-C(7D)	121.8(5)
C(2D)-C(7D)-C(6D)	117.9(4)
C(2D)-C(7D)-C(8E)	121.9(4)

C(6D)-C(7D)-C(8E)	120.2(4)
C(10D)-C(8D)-C(8E)	109.0(4)
C(7D)-C(8E)-C(8D)	113.4(4)
C(18D)-C(10D)-C(8D)	115.4(4)
C(18D)-C(10D)-C(1D)	111.7(3)
C(8D)-C(10D)-C(1D)	109.5(3)
O(2D)-C(11D)-O(1D)	124.0(4)
O(2D)-C(11D)-C(12D)	123.3(4)
O(1D)-C(11D)-C(12D)	112.7(4)
C(13D)-C(12D)-C(17D)	118.2(4)
C(13D)-C(12D)-C(11D)	117.5(4)
C(17D)-C(12D)-C(11D)	124.3(4)
C(14D)-C(13D)-C(12D)	122.1(4)
C(13D)-C(14D)-C(15D)	118.3(4)
C(16D)-C(15D)-C(14D)	121.3(4)
C(16D)-C(15D)-Br(1D)	119.6(3)
C(14D)-C(15D)-Br(1D)	119.1(3)
C(17D)-C(16D)-C(15D)	119.4(4)
C(16D)-C(17D)-C(12D)	120.7(4)
C(19D)-C(18D)-C(23D)	118.2(4)
C(19D)-C(18D)-C(10D)	119.8(4)
C(23D)-C(18D)-C(10D)	122.0(4)
C(20D)-C(19D)-C(18D)	121.0(5)
C(21D)-C(20D)-C(19D)	120.2(5)
C(22D)-C(21D)-C(20D)	119.7(4)
C(21D)-C(22D)-C(23D)	120.2(5)
C(18D)-C(23D)-C(22D)	120.7(4)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1A)	61(1)	43(1)	34(1)	22(1)	2(1)	-5(1)
O(1A)	23(2)	26(2)	28(2)	16(1)	5(1)	7(1)
O(2A)	27(2)	46(2)	37(2)	21(2)	6(1)	11(2)
C(1A)	24(2)	29(2)	27(2)	15(2)	0(2)	-2(2)
C(2A)	35(3)	29(3)	27(2)	13(2)	5(2)	-4(2)
C(3A)	42(3)	33(3)	31(3)	16(2)	7(2)	-4(2)
C(4A)	67(4)	39(3)	36(3)	12(3)	22(3)	2(3)
C(5A)	75(4)	50(4)	24(3)	9(3)	9(3)	-17(3)
C(6A)	53(3)	50(3)	28(3)	19(3)	-4(2)	-15(3)
C(7A)	37(3)	40(3)	32(3)	21(2)	-7(2)	-19(2)
C(8A)	30(2)	45(3)	36(3)	26(2)	-6(2)	-10(2)
C(9A)	25(2)	36(3)	47(3)	27(2)	0(2)	2(2)
C(10A)	28(2)	31(3)	34(3)	23(2)	3(2)	0(2)
C(11A)	24(2)	26(2)	24(2)	9(2)	0(2)	9(2)
C(12A)	27(2)	27(2)	23(2)	11(2)	3(2)	8(2)
C(13A)	37(3)	31(3)	34(3)	16(2)	5(2)	16(2)
C(14A)	50(3)	38(3)	48(3)	28(3)	4(3)	13(2)
C(15A)	39(3)	31(3)	26(2)	12(2)	-2(2)	-5(2)
C(16A)	32(3)	34(3)	34(3)	16(2)	5(2)	6(2)
C(17A)	31(3)	34(3)	34(3)	18(2)	5(2)	7(2)
C(18A)	29(2)	24(2)	36(3)	19(2)	0(2)	3(2)
C(19A)	29(2)	30(2)	34(3)	17(2)	5(2)	5(2)
C(20A)	49(3)	22(2)	40(3)	9(2)	0(2)	1(2)
C(21A)	50(3)	34(3)	31(3)	15(2)	4(2)	14(2)
C(22A)	41(3)	34(3)	38(3)	20(2)	16(2)	18(2)
C(23A)	27(2)	30(3)	37(3)	17(2)	3(2)	4(2)
Br(1B)	61(1)	42(1)	43(1)	28(1)	1(1)	9(1)
O(1B)	25(2)	31(2)	33(2)	21(2)	4(1)	5(1)
O(2B)	32(2)	69(3)	50(2)	41(2)	17(2)	19(2)
C(1B)	24(2)	32(2)	27(2)	18(2)	-1(2)	4(2)
C(2B)	31(2)	26(2)	21(2)	12(2)	-1(2)	4(2)

C(3B)	41(3)	38(3)	33(3)	17(2)	2(2)	-1(2)
C(4B)	52(3)	36(3)	40(3)	13(3)	-5(3)	-5(2)
C(5B)	60(4)	48(3)	30(3)	10(3)	1(3)	12(3)
C(6B)	36(3)	52(3)	32(3)	20(3)	5(2)	5(3)
C(7B)	36(3)	35(3)	23(2)	14(2)	1(2)	10(2)
C(8B)	28(2)	40(3)	31(2)	20(2)	3(2)	4(2)
C(9B)	25(2)	34(3)	34(3)	19(2)	4(2)	4(2)
C(10B)	24(2)	24(2)	31(2)	16(2)	2(2)	4(2)
C(11B)	32(3)	27(2)	20(2)	7(2)	5(2)	8(2)
C(12B)	27(2)	23(2)	21(2)	10(2)	2(2)	2(2)
C(13B)	33(2)	27(2)	28(2)	11(2)	10(2)	5(2)
C(14B)	40(3)	30(3)	26(2)	14(2)	6(2)	3(2)
C(15B)	35(3)	26(2)	30(3)	14(2)	1(2)	1(2)
C(16B)	33(3)	36(3)	36(3)	18(2)	4(2)	8(2)
C(17B)	35(3)	36(3)	30(3)	18(2)	12(2)	3(2)
C(18B)	27(2)	22(2)	32(2)	16(2)	3(2)	1(2)
C(19B)	29(2)	30(3)	34(3)	11(2)	-3(2)	3(2)
C(20B)	29(3)	37(3)	40(3)	12(2)	4(2)	6(2)
C(21B)	34(3)	33(3)	33(3)	10(2)	4(2)	8(2)
C(22B)	39(3)	35(3)	27(2)	12(2)	-7(2)	4(2)
C(23B)	28(2)	32(3)	40(3)	21(2)	0(2)	8(2)
Br(1C)	60(1)	39(1)	34(1)	13(1)	8(1)	14(1)
O(1C)	24(2)	27(2)	23(2)	6(1)	-1(1)	2(1)
O(2C)	24(2)	36(2)	51(2)	13(2)	-2(2)	2(1)
C(1C)	22(2)	24(2)	30(2)	11(2)	7(2)	3(2)
C(2C)	26(2)	30(2)	32(3)	16(2)	12(2)	8(2)
C(3C)	33(2)	31(3)	34(3)	15(2)	6(2)	5(2)
C(4C)	44(3)	42(3)	38(3)	23(3)	10(2)	16(2)
C(5C)	61(4)	33(3)	43(3)	22(3)	12(3)	10(3)
C(6C)	49(3)	28(3)	43(3)	14(2)	15(2)	2(2)
C(7C)	33(3)	29(2)	30(2)	8(2)	13(2)	9(2)
C(8C)	34(3)	30(3)	32(3)	10(2)	4(2)	1(2)
C(9C)	24(2)	35(3)	31(3)	11(2)	1(2)	-1(2)
C(10C)	28(2)	31(3)	25(2)	10(2)	4(2)	3(2)
C(11C)	24(2)	26(2)	31(3)	14(2)	0(2)	-1(2)
C(12C)	25(2)	22(2)	32(2)	13(2)	1(2)	-2(2)

C(13C)	32(2)	33(3)	35(3)	18(2)	-6(2)	0(2)
C(14C)	34(3)	34(3)	28(3)	13(2)	-5(2)	-3(2)
C(15C)	35(3)	29(2)	29(2)	16(2)	6(2)	4(2)
C(16C)	31(3)	37(3)	36(3)	22(2)	4(2)	3(2)
C(17C)	31(2)	32(3)	29(3)	17(2)	1(2)	2(2)
C(18C)	33(3)	34(3)	25(2)	12(2)	-2(2)	-2(2)
C(19C)	40(3)	45(3)	33(3)	19(2)	2(2)	1(2)
C(20C)	49(3)	63(4)	39(3)	30(3)	-5(3)	-16(3)
C(21C)	64(4)	42(3)	48(3)	25(3)	-24(3)	-14(3)
C(22C)	55(3)	41(3)	50(3)	25(3)	-11(3)	2(3)
C(23C)	40(3)	38(3)	45(3)	22(3)	-6(2)	0(2)
Br(1D)	61(1)	34(1)	31(1)	10(1)	-1(1)	-9(1)
O(1D)	23(2)	22(2)	26(2)	6(1)	4(1)	1(1)
O(2D)	22(2)	40(2)	43(2)	8(2)	9(1)	0(1)
C(1D)	23(2)	26(2)	23(2)	7(2)	-2(2)	-2(2)
C(2D)	34(3)	24(2)	24(2)	8(2)	-7(2)	-8(2)
C(3D)	34(3)	36(3)	28(3)	14(2)	-2(2)	-11(2)
C(4D)	55(3)	44(3)	38(3)	21(3)	-2(3)	-14(3)
C(5D)	65(4)	32(3)	40(3)	22(3)	-9(3)	-13(3)
C(6D)	57(3)	30(3)	38(3)	17(2)	-8(2)	1(2)
C(7D)	35(3)	28(2)	29(2)	13(2)	-6(2)	-2(2)
C(8D)	25(2)	32(3)	24(2)	9(2)	3(2)	5(2)
C(8E)	32(3)	29(3)	36(3)	11(2)	-4(2)	8(2)
C(10D)	27(2)	22(2)	24(2)	10(2)	1(2)	0(2)
C(11D)	25(3)	29(2)	27(2)	11(2)	6(2)	3(2)
C(12D)	25(2)	26(2)	27(2)	15(2)	3(2)	4(2)
C(13D)	24(2)	40(3)	35(3)	17(2)	6(2)	2(2)
C(14D)	36(3)	31(3)	34(3)	17(2)	8(2)	5(2)
C(15D)	39(3)	25(2)	26(2)	14(2)	4(2)	4(2)
C(16D)	24(2)	36(3)	34(3)	19(2)	-1(2)	-3(2)
C(17D)	28(2)	27(2)	31(3)	13(2)	4(2)	4(2)
C(18D)	26(2)	26(2)	25(2)	8(2)	1(2)	5(2)
C(19D)	33(3)	49(3)	34(3)	23(2)	9(2)	16(2)
C(20D)	49(3)	45(3)	36(3)	21(3)	7(2)	18(3)
C(21D)	72(4)	40(3)	48(3)	31(3)	25(3)	25(3)
C(22D)	62(4)	32(3)	50(3)	23(3)	14(3)	0(3)

C(23D)	34(3)	32(3)	38(3)	19(2)	4(2)	3(2)
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Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**.

	x	y	z	U(eq)
H(1AA)	8013	6298	4488	31
H(3AA)	8901	4880	3517	42
H(4AA)	8486	3867	2216	58
H(5AA)	5431	3843	1420	64
H(6AA)	2844	4823	1912	53
H(8AA)	2914	6520	3093	43
H(8AB)	1117	5812	3092	43
H(9AA)	2051	6189	4377	39
H(9AB)	1811	7065	4328	39
H(10D)	5769	7166	4214	34
H(13D)	8493	4246	5493	40
H(14D)	6932	3555	6163	50
H(16D)	1577	4896	6459	39
H(17D)	3035	5506	5704	38
H(19D)	8468	8004	5287	36
H(20D)	8966	9092	6550	47
H(21D)	6162	9256	7391	45
H(22D)	2950	8328	6961	42
H(23D)	2452	7237	5699	37
H(1BA)	12770	9329	9416	31
H(3BA)	13955	10795	10371	44
H(4BA)	13846	11854	11628	54
H(5BA)	10814	11806	12332	58
H(6BA)	8011	10705	11775	48
H(8BA)	5969	9599	10523	38
H(8BB)	7610	8973	10622	38
H(9BA)	6791	9202	9263	35
H(9BB)	6363	8332	9332	35
H(10C)	10292	8384	9606	30
H(13C)	13458	10323	7465	35

H(14C)	12102	11113	6861	38
H(16C)	6927	11630	8201	41
H(17C)	8191	10789	8764	39
H(19C)	12827	7629	8629	39
H(20C)	13054	6579	7379	44
H(21C)	10219	6313	6421	42
H(22C)	7195	7118	6721	41
H(23C)	6912	8155	7987	38
H(1CA)	19053	4322	-373	31
H(3CA)	20495	3802	538	39
H(4CA)	20464	2691	882	46
H(5CA)	17352	1690	508	52
H(6CA)	14369	1789	-227	48
H(8CA)	12286	2735	-622	40
H(8CB)	13764	2398	-1344	40
H(9CA)	13080	4134	-377	38
H(9CB)	12536	3624	-1296	38
H(10A)	16459	3508	-1422	35
H(13A)	20167	6506	2255	39
H(14A)	18939	7671	3287	40
H(16A)	13125	7324	1994	39
H(17A)	14360	6137	987	36
H(19A)	18872	4441	-1734	47
H(20A)	19115	5527	-2107	59
H(21A)	16361	6459	-1811	62
H(22A)	13403	6318	-1126	57
H(23A)	13263	5261	-717	48
H(1DA)	15180	11325	4207	31
H(3DA)	16323	11902	3303	40
H(4DA)	16240	13035	2988	55
H(5DA)	13411	13935	3373	53
H(6DA)	10744	13742	4116	50
H(8DA)	9066	11761	5088	34
H(8DB)	9233	11311	4170	34
H(8EA)	8701	12718	4504	41
H(8EB)	10574	13057	5210	41

H(10B)	13057	12015	5248	29
H(13B)	15360	9167	1615	40
H(14B)	13715	7957	551	39
H(16B)	8089	8150	1660	36
H(17B)	9714	9394	2700	34
H(19B)	15549	11060	5449	43
H(20B)	15684	9949	5784	50
H(21B)	12601	8964	5497	57
H(22B)	9402	9081	4854	56
H(23B)	9235	10207	4532	40

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⁷ This measurement is very different from that obtained in reference 4: $[\alpha]_{\text{D}}^{28} = +10$ (c = 1.2, EtOH) for compound **2** reported to have 96% ee.